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Mechanisms in Ruthenium(II) photochemistry and Iron(III) catalyzed oxidations

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Summary

In this thesis, photochemical, electrochemical and spectroscopic studies of Ru(II), Fe(II), and Fe(III) complexes are described. The overall goal in this studies was to understanding process that occur during oxidation catalysis and photo irradiation and especially the changes in the structure that take place.

Ligand oxidation or degradation is commonly observed during the catalytic oxidation of organic substrates with oxidants such as O_2 , H_2O_2 , and $tBuOOH$. Thus the role that ligand oxidation and changes in the coordination mode of catalysts play in both activating and deactivating catalysts during the oxidation of organic substrates is of interest. Several examples of ligand decomposition in iron, manganese, palladium, and ruthenium complexes are discussed in chapter 1. Ligand degradation or oxidation is typically considered as a route to deactivating a catalyst during oxidation reactions, however, several recent studies show that the pre-catalyst can converts to the active form period to the onset of the catalytic reaction. Therefore, although mechanistic studies and catalyst design focuses often on avoiding catalyst decomposition through the design of more robust ligands, activation/generation of the catalytically active species needs to be considered in catalyst development also.

The complex $[Fe(dppz)_2(NCS)_2] \cdot py$, which has been shown to exhibit spin state switching in the solid state through changes in temperature and/or pressure. In chapter 2, Light induced spin crossover in both the solid and dilute methanol solution was investigated using Raman spectroscopic techniques. A key challenge in the interpretation of the spectral data obtained is the non-innocence of the technique used to characterise the spin state, i.e. resonance Raman spectroscopy. Nevertheless, this technique is applied successfully to probe the spin crossover induced by the excitation laser used to obtain Raman spectra of the excited spin state. The TR^2 technique is used to monitor light induced spin state changes in this complex in solution. The LIESST effect is observed together with resonance enhancement of the Raman scattering of the low spin state at low temperature. A key finding, however, is that although the complex is viewed as being in the high spin state in the solid state at room temperature, it is clear from both UV-vis absorption spectroscopy and resonance Raman spectroscopy that in the solid state, in powder form, there is a substantial proportion of the complex in the LS state as well.

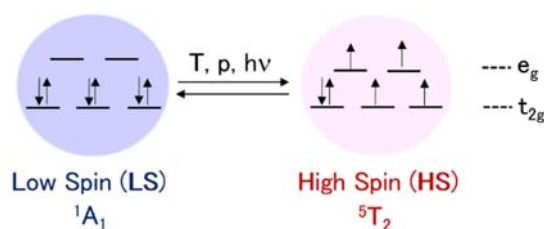


Figure 1. Electronic configuration of HS and LS states of d^6 ion, e.g., Fe(II), in an octahedral environment and spin crossover.

In chapters 3 and 4, attention turns to the discovery and development of new classes of photoswitches based on Ru(II) polypyridyl complexes based on metal centred photo induced ligand dissociation. A near completely reversible two-way photoswitching of the coordination mode in the complex $[\text{Ru}(\text{CH}_3\text{CN})(\text{MeN4Py})]^{2+}$ is observed in acetonitrile. Irradiation with visible light results in dissociation of a pyridyl unit attached via a $-\text{CH}_2-$ moiety to obtain a thermally stable photoproduct. the change is nearly fully reversed by photo-dissociation of the coordinated solvent molecule, that had filled the vacant coordination site, upon irradiation with near-UV light. In contrast, in the absence of the methyl group in the ligand backbone (i.e. with the ligand N4Py) two photoproducts in which the pyridine unit attached to $-\text{CH}-$ moiety is dissociated are obtained upon irradiation. The combination of ^1H NMR spectroscopy, ESI mass spectrometry and X-ray crystallography enabled identification of the photoproducts, which are isomers differing in the arrangement of the $-\text{CH}_2-$ pyridyls, *cis* and *trans* to each other. The minor difference between a hydrogen and a methyl group in the ligand backbone is remarkable with a highly reversible and selective dissociation of the least sterically hindered $-\text{CH}_2-$ pyridyls with a methyl group, while in the absence of methyl group two thermally stable isomers are formed, highlighting the Thorpe-Ingold effect and the delicate balance in dissociation of the pyridyl rings. These photoproducts, which are not accessible through thermal chemistry, are of interest in future studies in the catalytic oxidation of organic compounds and also open up new opportunities in the fields of inorganic photochemistry.

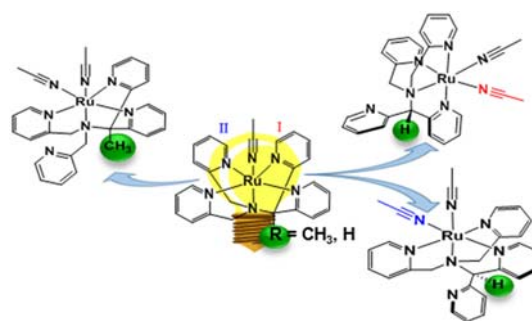


Figure 2. Photo induced ligand dissociation in $[\text{Ru}(\text{CH}_3\text{CN})(\text{MeN4Py})]^{2+}$ and $[\text{Ru}(\text{CH}_3\text{CN})(\text{N4Py})]^{2+}$ upon irradiation with visible light.

In chapters 5 and 6, attention turns to an Fe(III) based complex that has been applied earlier in the catalytic oxidation of benzyl alcohols and is typical of pyridyl/phenolato based complexes. In chapter 5 the electropolymerization of the complex due to the redox chemistry of the phenol unit of the μ -oxo-diiron(III) complex $[(\text{L}^1)\text{Fe}(\mu\text{-O})\text{Fe}(\text{L}^1)]^{2+}$ is demonstrated. The phenoxyl radical generated both electrochemically and with chemical oxidation ($\text{Ce}(\text{IV})$) was followed by C-C bond formation to form a *tetranuclear* complex without the breakup of the μ -oxo bridging unit. The polymer films formed on electrodes were characterized by voltammetry, UV-vis absorption, and resonance Raman spectroscopy, to determine the oxidation state of the polymer. Notable, the electropolymerization of the phenolate ligand (L^1) is not observed, which indicates that this system has a potential in controlling oxidative coupling of phenol units through complexation with Fe(III).

In chapter 6, a spectroscopic study of these Fe(III)-phenolate complexes under catalytic conditions, i.e. in the oxidation of benzyl alcohol, is reported. The complex was applied earlier as a catalyst for alcohol oxidation, however, the mechanism and especially the role of acid in this chemistry were not clarified. The combination of UV-vis absorption, ^1H NMR, EPR, ESI mass, and Raman

spectroscopies indicated that degradation of phenolato ligand occurred in the presence of excess H_2O_2 to form an N3Py type ligand coordinated to the iron complex and it is this species that is catalytically active. Although the precise structure of the intermediate species was not revealed, the realization that the phenolato unit is lost prior to the onset of catalytic activity is essential to gain an understanding of the role of phenolato based catalysts in catalytic oxidations. The electrochemical and spectroscopic studies in chapter 5 provided a spectroscopic database that proved that C–C coupling of phenoxyl radical species can occur upon oxidation with H_2O_2 , however, under catalytic conditions resonance Raman spectroscopy with high time resolution shows that this process is not relevant to catalytic oxidation due to the much more rapid cleavage of the phenol unit in the presence of H_2O_2 . Importantly, acid does not in fact accelerate the catalytic reaction by breaking up the μ -oxo bridge. DFT, and spectroscopic data indicate that the role of acid is in fact to facilitate initial electron transfer oxidation with H_2O_2 . The challenge undertaken in this chapter was to combine several techniques in the identification of intermediate or transition species and also to understand the mechanism by which these catalysts operate. This understanding is essential to future ligand design efforts incorporating redox active phenol based ligands with oxidation catalysts.

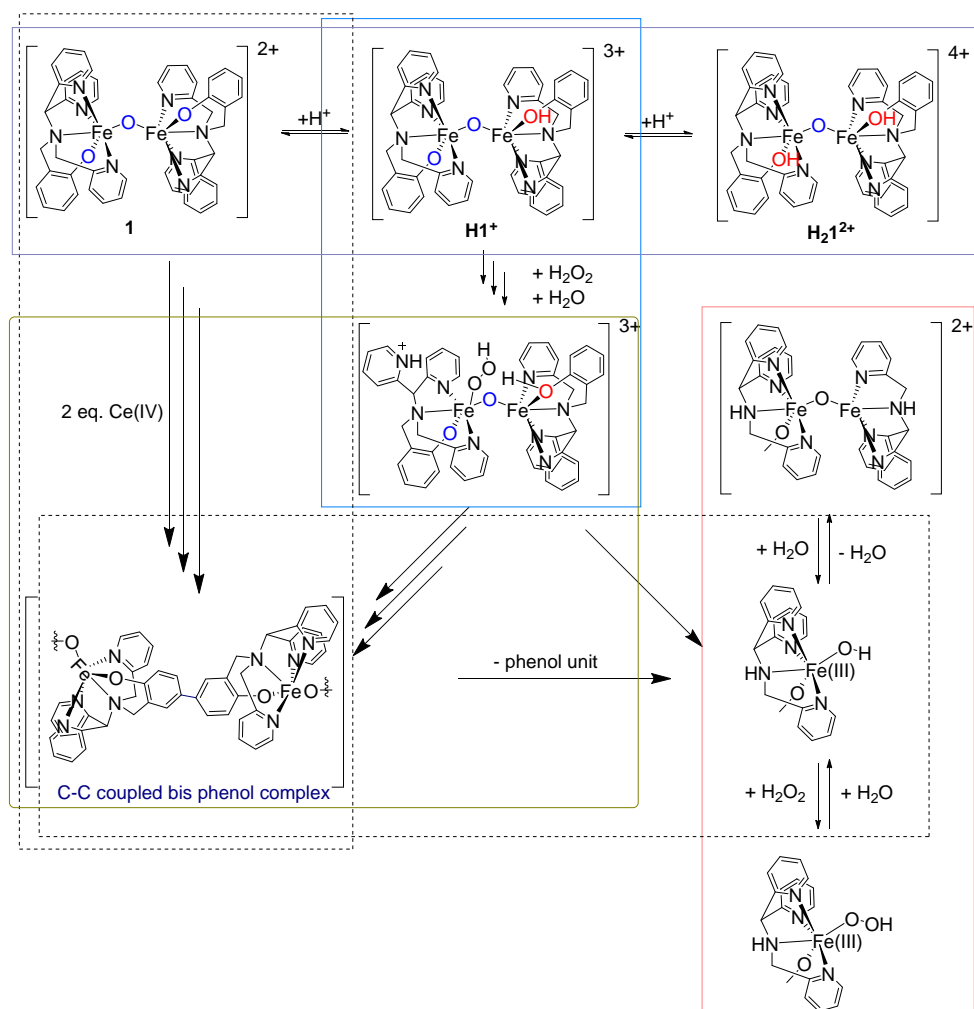


Figure 3. Summary of processes observed for **1** in solution upon oxidation with stoichiometric H_2O_2 and with excess H_2O_2 .

